

LEAD SULFATE SCINTILLATOR CRYSTAL GROWTH FOR PET APPLICATIONS

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Abstract*

It has recently been shown that lead sulfate (PbSO_4) is a promising scintillator material for use in PET detector systems. However, for lead sulfate scintillators to be useful in such an application, a technique must be developed to grow large optical quality crystals of this material. This paper describes our research into the high-temperature solution growth of PbSO_4 crystals. We report on the systematic selection of solvent materials including KCl , LiCl , PbCl_2 , Na_2SO_4 and Li_2SO_4 . Our studies indicate that Na_2SO_4 is the best solvent. With Na_2SO_4 as the flux, we obtained PbSO_4 single crystals of several millimeters in size by Bridgman crystal growth method. We employed ACRT (Accelerated Crucible Rotation Technique), to resolve the constitutional supercooling problem, thus increased the crystal yield and reduced the number of grains. Finally, we compared the scintillation properties of synthetic PbSO_4 crystals we grew with previous measurements on natural anglesite and other synthetic crystals, and found them nearly identical.

I. INTRODUCTION

The properties of an ideal scintillator for use in PET applications have long been known to be: high photon stopping power (high Z), high light yield and fast decay speed. There has been a great deal of recent interest in finding new scintillators for PET which have properties superior to the scintillators currently in use (mainly BGO). Recently, the scintillating properties of PbSO_4 crystals have been investigated [1, 2 and 3] and found to show considerable promise due to their high average atomic number (72), reasonably high light output (60% of BGO), fast response of about 3 times faster than BGO (5% @ 1.8 ns, 36% @ 19 ns, 36% @ 95 ns and 23% @ 425 ns), environmental stability (non-hygroscopic, hard), and high density (6.4 g/cm^3). However there is no known method

for growing large, clear crystals of PbSO_4 , which is necessary if this material is to be used for PET. Thus the central question to be answered is whether high quality crystals of this material can be prepared synthetically and, if so, are the scintillation properties of the synthetic crystals different than those of natural anglesite?

II. LEAD SULFATE CRYSTAL GROWTH

PbSO_4 has a melting point of 1170°C. It decomposes, however, at 900°C and has a solid-solid phase transition at 856°C from monoclinic to orthorhombic [4]. This phase transition would create severe strain or even fracturing in the growing crystal. Thus, the conventional techniques of direct growth from a melt, such as Bridgman or Czochralski, are not suitable for growing PbSO_4 crystals.

Historically, several attempts had been made to synthesize PbSO_4 crystals by gel growth methods [5, 6] and high temperature solution growth methods [7, 8]. These attempts have produced small crystals of poor optical quality which were unsuitable for scintillation testing. More recently, samples of PbSO_4 have been grown by the hydrothermal method [9]. In this paper we report on a variation of high temperature solution growth using the flux Bridgman growth and Accelerated Crucible Rotation Technique (ACRT) assisted flux Bridgman growth.

III. FLUX BRIDGMAN GROWTH

In this method, the constituents of PbSO_4 are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The principal advantage of using a solvent is that PbSO_4 crystal growth may occur below the destructive solid-solid phase transition [10]. Using Na_2SO_4 as a solvent, for instance, one may reduce PbSO_4 solidification point from 1077°C to 730°C by adjusting $\text{PbSO}_4/\text{Na}_2\text{SO}_4$ ratio towards relatively sodium rich side, based on system $\text{PbSO}_4/\text{Na}_2\text{SO}_4$ phase diagram (figure 1)[11]. Thus PbSO_4 crystals are able to precipitate from the liquid solution between 856 and 730°C, (above 900°C decomposition and at 856°C solid phase transition). It is very clear that an appropriate solvent is critical in achieving a high quality PbSO_4 single crystal from solution.

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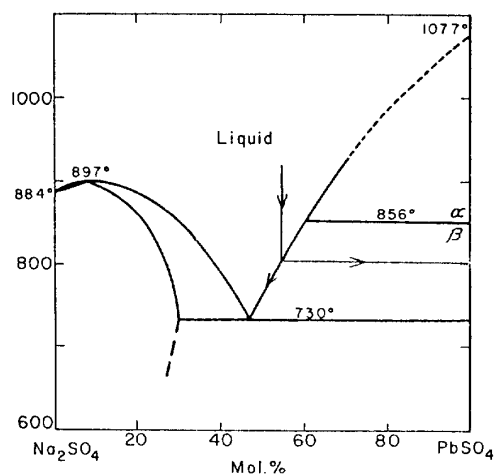


Figure 1. Phase diagram for the system $\text{PbSO}_4/\text{Na}_2\text{SO}_4$, where α phase is monoclinic and β phase is orthorhombic structure. (Adapted from C. Perrier and A. Bellanca, *Periodica Mineral.* vol. 11, pp. 189, 1940)



Figure 2. Multiple small PbSO_4 crystals obtained from the tip of an ingot grown in $\text{PbSO}_4/\text{Na}_2\text{SO}_4$ system. The initial composition was 55% PbSO_4 and 45% Na_2SO_4 . The scale is in millimeters.

A. Solvent Selection

Preliminary solvent-selection experiments were conducted using five types of solvent materials including: KCl , LiCl , PbCl_2 , Na_2SO_4 and Li_2SO_4 .

In these experiments, each flux material was well mixed with an appropriate amount of PbSO_4 according to the phase diagrams [11, 12, 13 and 14] and loaded into individual alumina crucibles. The mixed chemicals were subsequently melted and slowly dropped out (5 mm per day) of a Bridgman furnace. The tips, near the bottom of the crucibles, and the ends, near the top of the crucibles, of grown ingots were cut off and examined under a microscope and with X-ray diffraction.

For the ingots with initial compositions of 55% PbSO_4 and 45% Na_2SO_4 , and of 60% PbSO_4 and 40% Li_2SO_4 , the tips appeared to be pearlescent and translucent. The crystal/flux interface can be very clearly observed in the ingot formed in the $\text{PbSO}_4/\text{Na}_2\text{SO}_4$ system. The tip of a typical ingot contains multiple crystals as shown in figure 2. X-ray diffraction patterns confirmed that the tip is PbSO_4 (Fig. 3a) while the end contains both PbSO_4 and Na_2SO_4 (Fig. 3b). For the ingot formed in the $\text{PbSO}_4/\text{Li}_2\text{SO}_4$ system, the data reveals that the tip contains mainly PbSO_4 with a small amount of Li_2SO_4 (Fig. 3c), while the end contains mainly Li_2SO_4 with some PbSO_4 (Fig. 3d).

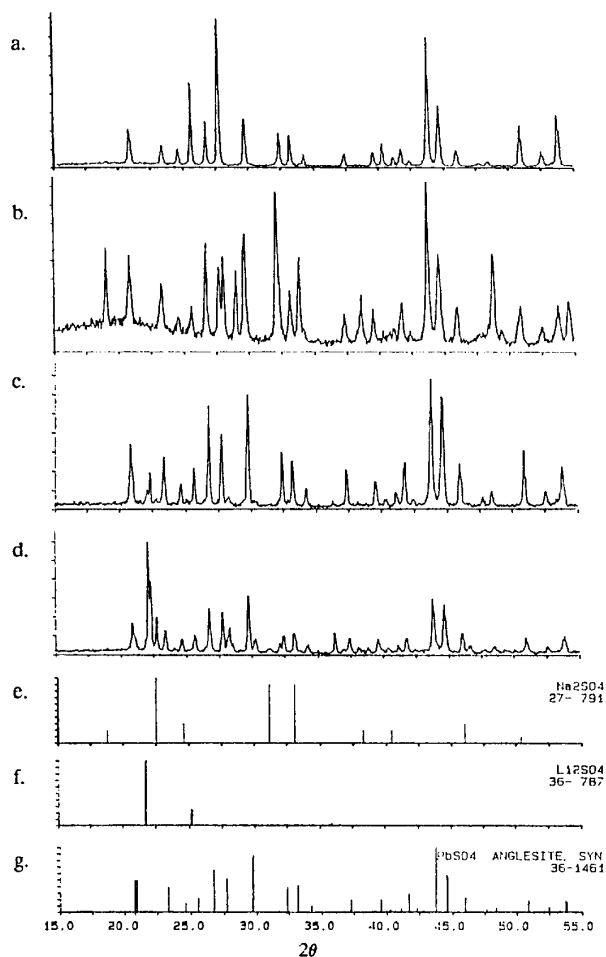


Figure 3. X-ray diffraction data of $\text{PbSO}_4/\text{Na}_2\text{SO}_4$ system indicate that (a) the tip of ingot contains only PbSO_4 , (b) the end of ingot contains both Na_2SO_4 and PbSO_4 ; x-ray diffraction data of $\text{PbSO}_4/\text{Li}_2\text{SO}_4$ system indicate that (c) the tip of ingot contains mainly PbSO_4 with a small amount of Li_2SO_4 , (d) the end of ingot contains mainly Li_2SO_4 with some PbSO_4 . The JCPDS standards [15] of PbSO_4 , Na_2SO_4 and Li_2SO_4 are included in (e), (f) and (g), respectively, for comparison.

For the ingots formed with initial compositions of 20% KCl with 80% PbSO_4 , 80% PbCl_2 with 20% PbSO_4 and

20% LiCl with 80% PbSO₄, the tips appeared to have either a chalky or opaque luster with vitreous grains. Furthermore, X-ray diffraction patterns confirmed that the tips contain not only PbSO₄, but also significant amounts of PbCl₂, Li₂SO₄, KCl, LiCl, K₂SO₄ or combinations of these compounds.

Therefore, the experimental results conclusively ruled out the possibility of utilizing PbCl₂, KCl or LiCl as flux materials to grow PbSO₄ crystals. Residual Li₂SO₄ remained in the grown crystal when it was used as the flux. We chose Na₂SO₄ as the flux material.

B. Crystal Growth

According to Perrier and Bellanca (figure 1), the thermodynamically stable range permitting the growth of a PbSO₄ crystal in a PbSO₄/Na₂SO₄ system is located within approximately 47 to 61 mole percent of PbSO₄ with 53 to 39 mole percent of Na₂SO₄ flux, corresponding to its solidification temperature of 730 to 856°C, respectively. In this system, 730°C is a eutectic point which is thermodynamically unstable; while beyond 856°C, a high temperature monoclinic phase, should also be avoided.

Accordingly, we started flux growth of PbSO₄ at about 46 to 54 mole ratio of Na₂SO₄ to PbSO₄. The corresponding solidification temperature was about 800°C. The Bridgman method was used at a growth rate of 5 mm/day, and temperature gradient of 15 °C/cm. With such an experimental set up, the largest single crystal grain recovered from the grown boule was approximately 3 mm x 4 mm x 6 mm. In general, however, the crystal grains were still small.

Subsequent examination of the crystals produced by the Bridgman method indicated that significant amounts of solvent were trapped in the lead sulfate boule. In addition, the growth morphology indicated that constitutional supercooling had occurred. To minimize these problems we elected to use the ACRT to stir the solution in all subsequent growth attempts [16 and 17].

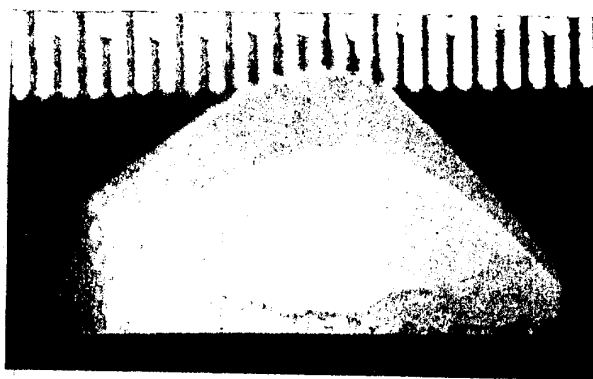


Figure 4. PbSO₄ crystal cut from a boule grown by ACRT assisted Bridgman flux growth. The scale is in millimeters.

Our first ACRT Bridgman growth did not produce any PbSO₄ crystal because a sinusoidal rotation pattern (angular velocity versus time) was used. In the second ACRT attempt, a triangular rotation pattern (linear acceleration with fast reversal of ampoule rotation direction) was used. This second ACRT attempt produced a crystal boule containing our largest single grain of approximately 5 mm x 6 mm x 8 mm shown in figure 4. These results are consistent with the results obtained by others, implying that rapid acceleration/deceleration is the most critical part of the ACRT technique while stop time, run time at a constant rate and rotation reversal are of less importance [17].

IV. CRYSTAL CHARACTERIZATION

A. PbSO₄ Crystal Yield

In an ideal flux growth of PbSO₄, one would start with 46 mole percent of Na₂SO₄ and 54 mole percent of PbSO₄. When the PbSO₄ crystal starts to grow, the concentration of solution shifts towards the sodium rich side. Assuming diffusion is sufficient, when the concentration of solution reaches the eutectic point, 53 mole percent of Na₂SO₄ with 47 mole percent of PbSO₄, crystallization of two solid phases (PbSO₄ and Na₂SO₄) occurs. Thus growth of single phase PbSO₄ effectively ends. With this system, it can be estimated that the PbSO₄ crystal yield can reach 27 percent of its original concentration in solution. However, in a regular Bridgman flux growth the weight of the PbSO₄ crystal recovered only represents a yield of about 19%, while in the ACRT assisted Bridgman flux growth the yield exceeded 23%. The difference between estimated values and experimental data could be easily understood by assuming that an unstable growth condition occurred in the process due to insufficient mass diffusion. Constitutional supercooling, cellular growth and, consequently, dendritic growth were identified in the grown ingot.

B. Constitutional Supercooling

A polished slice of the crystal, from a Bridgman solution grown boule, cut perpendicular to the growth axis is shown in the photograph of figure 4. The multiple grain boundaries at the right side of the photograph, corresponding to near the edge of the crystal, clearly showed an irregular cellular interface structure characteristic of the starting point of constitutional supercooling. The dendrites with Na₂SO₄ flux residuals (white powder-like) at the left side of the photograph, corresponding to the center part of the crystal, revealed further development of such constitutional supercooling. Here, because of the growth temperature profile, the solid/liquid interface observed is concave. Thus the constitutional supercooling occurred from the tip of the boule to the end, and radially as well. See the illustration

in figure 5.

a.



b.

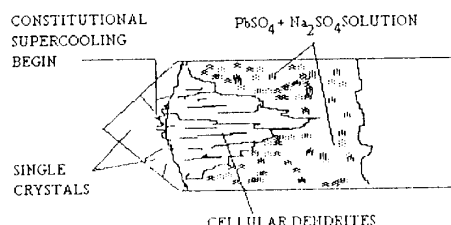


Figure 5. (a) Photograph of a polished slice of PbSO_4 cut from a crystal grown by the Bridgman solution growth method. The slice was cut perpendicular to the growth axis. Evidence of constitutional supercooling can be seen near the edge of the crystal, (right side of photo); and dendritic growth with residual Na_2SO_4 flux can be seen near the center of the crystal, left side of the photo.

(b) Drawing illustrates the various structures developed in an ingot.

It is worthwhile to point out that the type of cellular interface structure [18] we observed has been observed by others to occur when growth conditions are close to those required for formation of a smooth interface and significantly larger grains. The constitutional supercooling condition is sensitive to the growth parameters of: temperature profile in the melt, crystal growth rate and ampoule rotation acceleration and deceleration pattern.

C. Crystal Size

Although PbSO_4 crystals several millimeters in size were obtained with our experiments, most scintillation applications require significantly larger size single crystals. We observed that multiple grain boundaries and cracks in the single grains confined the size of single crystals being grown. The case of the multiple grains may also be caused by constitutional supercooling, which turns normal crystal growth into cellular growth. At this transition region multiple grains grow together. The destructive force among these multiple phases may penetrate into the single

grains. Thus, very few crystal grains may survive after cellular growth and secondary cracks have developed.

D. Crystal Inclusions

It has been reported that the natural PbSO_4 crystals (anglesite) from a number of different locations, yielded a wide variation in the total light output mainly due to imperfections in the crystals. Previous attempts at growing lead sulfate crystals from high temperature solution also resulted in crystals of poor optical quality due to numerous inclusions of the flux materials [3].

The crystals we grew were observed by optical microscopy to determine the extent of inclusions and bubbles which might adversely effect the optical properties of the crystal. In a cut and polished sample of PbSO_4 crystal grown from the first ACRT assisted Bridgman flux growth, we still observed some gas bubble-like inclusions as shown in figure 6. The density of inclusions was estimated to be about 300 per square centimeter for this sample. Similar bubble densities were previously measured from regular Bridgman flux grown PbSO_4 crystals. So far, there is no sufficient data to support whether the ACRT method reduces the number of such bubbles. Characterizing impurity inclusions in grown crystals by techniques such as chemical trace analysis as well as relative measurement of light output remains to be done. These measurements will help to answer whether impurities which degrade the scintillation performance come from the original raw materials, the flux process or the crucible.

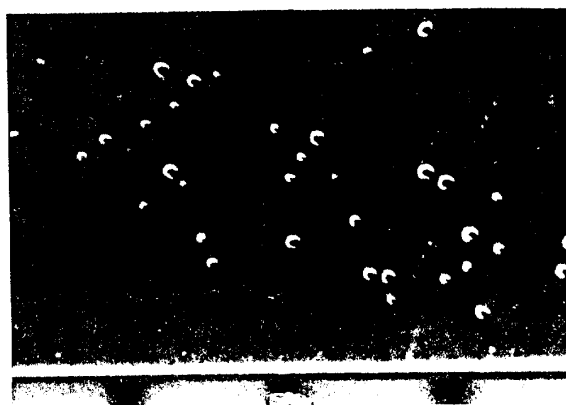


Figure 6. Gas bubble like inclusions in a polished slice from an ACRT assisted flux Bridgman grown PbSO_4 crystal sample.

V. SCINTILLATION PROPERTIES

Preliminary data on the scintillation properties of both Bridgman grown crystals and ACRT grown PbSO_4 crystals were measured and compared to previous measurements. Three types of scintillation measurements were performed: pulse height spectra when irradiated from an isotopic source, optical emission intensity spectra and decay time.

The pulse height data were obtained by polishing samples of the crystals and mounting them to a 1 cm Hamamatsu R-1635 photomultiplier tube. The remaining sides of the crystals were coated with white Teflon reflective tape. The crystals were irradiated with a ^{22}Na source. The photomultiplier tube signal was shaped and amplified by a Canberra 2020 spectroscopy amplifier ($4\ \mu\text{s}$ shaping time) and the pulse height spectra were accumulated with a Nucleus PCA-1000 card installed in a PC. Some results are shown in figures 7 and 8.

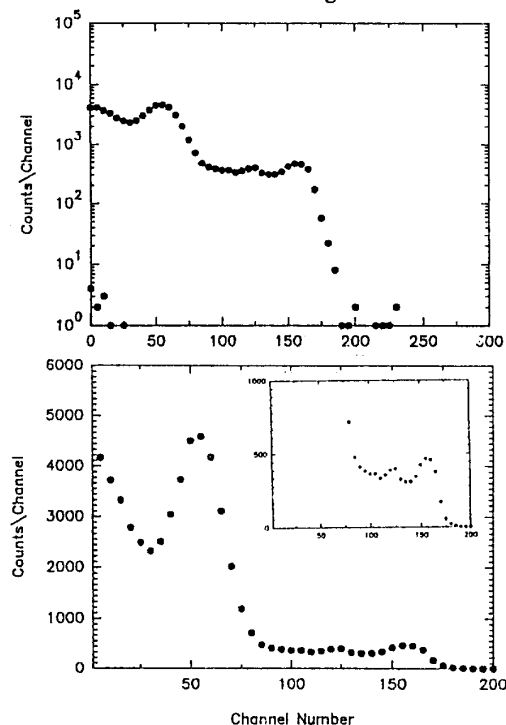


Figure 7. Pulse height spectra of ^{22}Na from an ACRT Bridgman flux grown PbSO_4 crystal of 4 mm x 5 mm x 6 mm. Upper figure is log scale, lower figure, where 1.275 MeV photo peak is also included, is linear.

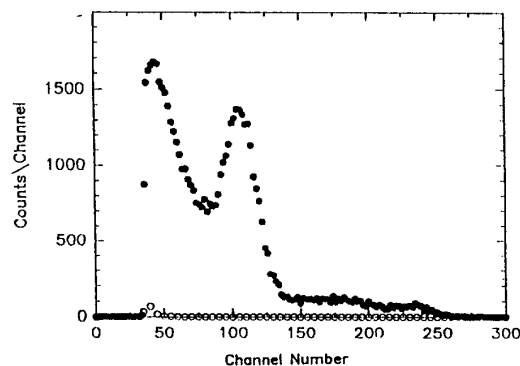


Figure 8. For another small crystal (2 mm x 3 mm x 4 mm), an energy resolution of 35% was obtained for the 511 keV peak.

We observed that the photopeak spectra from synthetic PbSO_4 crystals were remarkably similar to those which were obtained with natural anglesite [3], implying that the light output of the synthetic crystals is probably similar to the natural material. However it is potentially capable of being improved by reducing synthetic crystal imperfections.

The optical emission spectrum and scintillation decay time properties of these synthetic PbSO_4 crystals were measured using the same method described in [3], and compared with those previous measurements, which were made with small (<1 mm) PbSO_4 crystals grown from an aqueous PbCl_2 solution [7]. The optical emission spectrum, corrected for the spectral response of the monochromator and photomultiplier tube, is shown in figure 9, and is indistinguishable from previous measurements.

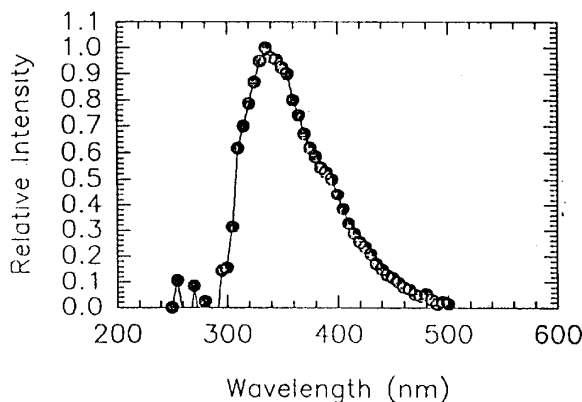


Figure 9. Optical emission spectrum of a synthetic PbSO_4 crystal grown from flux Bridgman.

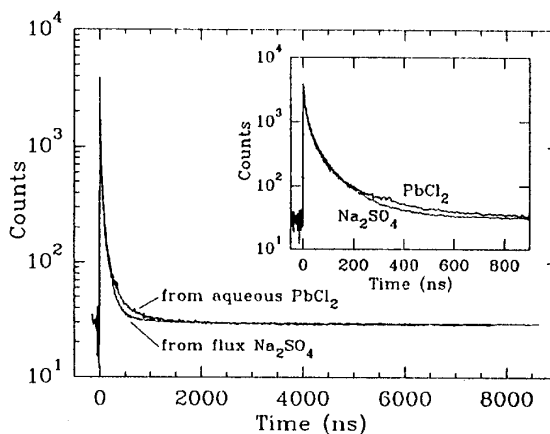


Figure 10. Decay time spectra of a synthetic PbSO_4 crystal grown from flux Bridgman and from aqueous PbCl_2 solution.

The scintillation decay time spectra of the present and previous PbSO_4 crystals are shown in figure 10. For all practical purposes, the shapes of the two decay curves are identical, although the crystals grown from Na_2SO_4 flux exhibit a slightly faster decay time than those grown from

aqueous PbCl_2 solution. When the present data is fit to a sum of 5 exponential decay components, we find that most of the light is "fast" (1.5% @ 0.40 ± 0.02 ns, 21% @ 7.2 ± 0.1 ns, 32% @ 35 ± 1.0 ns, and 39% @ 104 ± 2.0 ns), but there is a small "slow" component (5.5% @ 656 ± 38 ns).

VI. CONCLUSION

Crystals of lead sulfate were grown using a variation of the high temperature solution growth method. Some of the scintillation properties of these crystals were measured. The scintillation properties were found to be very similar to those obtained from the natural crystals of anglesite and crystals grown from aqueous PbCl_2 solution.

Although high-temperature solution growth of PbSO_4 using Na_2SO_4 as the solvent has proven to be very promising, there is still room for significant improvement. Problems such as a large number of grains, low yield, dendritic solidification, and numerous inclusions were mainly caused by constitutional supercooling, due to insufficient mass transport at the crystal growth interface. Therefore, for future advances in growing large optical quality single PbSO_4 crystals, a growth condition which maintains a well mixed fast solution flow at the growth layer must be achieved.

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